Enhancing Performances of Perovskite Solar Cells by Using Zinc Oxide Quantum Dots/Mesoporous Titania Electron Transport Layer

Mei Wang

Hubei University of Technology

Huating Bo

Hubei University of Technology

Qiuyun Fu (✉ fuqy@mail.hust.edu.cn)

Huazhong University of Science and Technology

Xinguo Ma

Hubei University of Technology

Zhengwang Cheng

Hubei University of Technology

Jing He

Hubei University of Technology

Wei Zou

Hubei University of Technology

Research Article

Keywords: mesoscopic perovskite solar cells, surface modification, quantum dots, electron extraction, specific surface area

Posted Date: June 12th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-607253/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Enhancing Performances of Perovskite Solar Cells by Using Zinc Oxide Quantum Dots/Mesoporous Titania Electron Transport Layer

Mei Wang[†], Huating Bo[†], Qiuyun Fu^{‡}, Xinguo Ma[†], Zhengwang Cheng[†], Jing He[†],
Wei Zou[†]*

[†] Hubei Engineering Technology Research Center of Energy Photoelectric Device and System, Hubei University of Technology, Wuhan 430068, P. R. China

[‡] School of Optical and Electronic Information, Engineering Research Center for Functional Ceramics of the Ministry of Education, Huazhong University of Science and Technology, Wuhan 430074, P. R. China

* Corresponding author: fuqy@mail.hust.edu.cn

Abstract

As the photovoltaic performance of mesoscopic perovskite solar cells (PSCs) is strongly dependent on the interface between perovskite and electron transport layer. Herein, an attempt to load facile processed ZnO quantum dots (ZQDs) or TiO₂ quantum dots (TQDs) into the mp-TiO₂ layer via a simple spin-coating method was first performed. Both of them had huge impact on the morphology of perovskite films, leading to larger perovskite grains. However, the power conversion efficiency (PCE) of these two kinds of QDs modified cells exhibited a different tendency. The champion PCE of ZQDs modified PSCs was remarkably improved from 14.54% to 17.2%, while that of TQDs modified ones decreased to 11.78%. We demonstrated that the enhanced PCE and short-circuit current (J_{sc}) were attributed to the enlarged grain size and enhanced light absorption of perovskite film, faster electron extraction and transport as well as less recombination for ZQDs modified PSCs, which mainly resulted from the increased active specific surface area. On the contrary, deterioration of TQDs modified PSCs was exactly ascribed to the aggregation of TQDs which sharply decreased the

specific surface area of the electron transport layer. The current work provided an efficient and facile way to improve the photovoltaic performance of mesoscopic PSCs.

Keywords: mesoscopic perovskite solar cells, surface modification, quantum dots, electron extraction, specific surface area

1. Introduction

Since the organometal trihalide perovskite were reported as photosensitizers for photovoltaic cells,¹ they have attracted great attention for their low cost, simple manufacturing process and high photovoltaic performance in the field of optoelectronics, especially in the application of perovskite solar cells (PSCs).² The energy conversion efficiency of PSCs has risen from 3 %¹ to 25.5 %³ in just a few years.

Mesoporous structured PSCs, especially those based on mesoporous TiO₂ (mp-TiO₂), have been proved to have the highest power conversion efficiency (PCE). Because the mp-TiO₂ has a large specific surface area, it can be used as a scaffold to increase the loading amount of perovskite. In addition, it is in direct contact with perovskite and acts as an electron transport layer (ETL), collecting photoelectrons from perovskite and transmitting them to the front contact.^{4, 5, 6} Therefore, it will be a possible way to promote the performance of PSCs by increasing the effective specific surface area between the carrier transport layer and the light absorbing layer.^{7, 8, 9, 10, 11}

Due to the fact that quantum dots (QDs) are only a few nanometers in diameter, they are endowed with large specific surface area. Additionally, due to the influence of quantum confinement effect and edge effect, the band gaps of QDs are adjustable. These characteristics make them possess potential application prospect in the field of PSCs. For instance, in planar heterojunction PSCs, black phosphorus QDs have been used to enhance the hole extraction.¹² CdSe QDs, graphene QDs and Carbon QDs have respectively been used to modify the ETL to make the perovskite thin films denser or accelerate the extraction rate of electrons.¹³⁻¹⁵ According to this idea, selecting

appropriate quantum dots to modify the mp-TiO₂ is expected to obtain an idea carrier transport material with large specific surface area, appropriate energy level and high conductivity.

In this thesis, we plan to prepare ZnO QDs (ZQDs) and TiO₂ QDs (TQDs), embedding them into mesoporous scaffolds to increase the specific surface area of mesoporous layer, and finally enhance the light absorption of perovskite layer and accelerate the extraction and transmission of electrons. On the one hand, ZnO and TiO₂ have ever been employed as excellent ETL in the area of PSCs owing to their suitable energy levels. On the other hand, ZQDs and TQDs are easily synthesized, and they can be deposited into mesoporous layer by simple spin coating technique. In addition, ZnO has a high electron mobility of 115–155 cm² V⁻¹ s⁻¹,^{16, 17} which is favorable for electron transport.

With this strategy, ZQDs and TQDs modified mesoscopic PSCs have been prepared. Unexpectedly, the ZQDs modified mesoscopic PSCs showed an enhancement in PCE (PCE=17.20%) as compared to unmodified PSCs (PCE=14.54%), while TQDs modified ones showed an opposite tendency (PCE=11.78%). Further discussions indicated that enhanced light absorption, accelerated electron transport, extraction and less recombination were existed in ZQDs modified PSCs for their increased surface area. On the contrary, because of the aggregation of TQDs on the mp-TiO₂, the pore volume and specific surface area were sharply decreased which ultimately led to the performance deterioration of the TQDs modified PSCs.

2. Results and discussion

PSCs with the structure of FTO / blocking TiO₂ (BL) / bare or QDs modified mp-TiO₂ / CH₃NH₃PbI₃ (MAPbI₃) / hole transport material (HTM) / Au were fabricated. The fabrication process of PSC modified by QDs is shown in Figure 1.

Figure 1. Fabrication process of QDs modified PSCs.

Figure 2. XRD testing results of (a) ZQDs and (b) TQDs; TEM and HRTEM (inset) image of (c) ZQDs and (d) TQDs; (e) distribution of Zn in ZQDs/mp-TiO₂ sample obtained from the cross section-scan analysis of EDS mapping images and the corresponding cross section SEM image.

Figure 2a, b represent the X-ray diffraction (XRD) patterns of ZnO and TiO₂ powders obtained by drying solution, which correspond to the hexagonal wurtzite zinc oxide (JCPDS #36-1451) and the anatase titanium dioxide (JCPDS#01-0562),

respectively, without any impurities observed. The evidently broad nature of reflections confirms that particles are in nanoscale. According to the Debye Scherer formula $D=0.89 \lambda / (\beta \cos \theta_B)$, where D represents the diameter of particles, λ represents the x-ray wavelength (1.5406 Å), θ_B represents the Bragg diffraction angle, and β represents the peak width at half maximum, the calculated grain size of ZnO and TiO₂ are about 6 nm and 7 nm, respectively, indicating the formation of QDs. Transmission electron microscopy (TEM) images (Figure 2c, d) reveal that both the as-prepared ZQDs and TQDs are well-distributed and nearly spherically shaped dots with an average diameter of about 5 nm. High-resolution TEM (HRTEM) image of ZQDs shows the lattice distance of 0.282nm and 0.265nm, corresponding to the (101) and (002) facets. As for the TQDs, a lattice spacing of 0.352 nm is taken, which is corresponded to the (101) facets of TQDs. Then the as-prepared ZQDs or TQDs were added by spin coating their dispersion solution onto the mp-TiO₂ layers. SEM (scanning electron microscope) and EDS (energy dispersive spectrometer) mapping images shown in Figure 2e indicate a homogeneous distribution of ZQDs in mp-TiO₂ matrix.

Figure 3. Diagram of energy levels in the ZQDs or TQDs modified device.

To verify whether the QDs can work well in the devices, the surface energies were characterized by UV-vis absorption spectrum and Ultraviolet photoelectron spectroscopy (UPS) (Figure S1). According to the absorption spectra, the band gaps are 3.34, 3.40, 4.05 eV for mp-TiO₂, ZQDs and TQDs, respectively, which are depending on the wavelengths of onset absorption. The valence band maximum

(E_{VB}), taken from the UPS, calculated using the expression $E_{VB} = -(21.22\text{eV} - E_{\text{cut-off}} + E_{\text{fermi}})$, are -7.32, -7.4 and -8.0 eV for mp-TiO₂, ZQDs and TQDs, respectively. The conduction band minimum (E_{CB}) are calculated to be -3.98, -4.0 and -3.95 eV for mp-TiO₂, ZQDs and TQDs, respectively, referring to the expression $E_{CB} = E_{VB} + \text{band gap}$. The band scheme of the mp-TiO₂, ZQDs, TQDs, MAPbI₃ and HTM are depicted in Figure 3, from which we can see that both energy levels of ZQDs and TQDs match well with the mp-TiO₂ and perovskite.

Figure 4. Top-view FESEM images of perovskite crystals grown on (a) the pristine mp-TiO₂, (b) the ZQDs modified mp-TiO₂ and (c) the TQDs modified mp-TiO₂ film; Cross-sectional SEM images of a complete device based on the (d) PT, (e) PZT and (f) PTT structure. Insets are the grain size distributions of perovskite. The scale bars for all SEM images are 200 nm.

Figure 5. XRD testing results of perovskite films on original TiO₂, the ZQDs treated TiO₂ and the

TQDs treated TiO₂ layer.

The MAPbI₃ films were formed by spin coating the perovskite precursor solution on the bare or QDs modified mp-TiO₂ substrate and then heating at 100°C for 2 min. Figure 4, a, b, c display the field emission scanning electron microscope (FESEM) top-view images of the perovskite films on the bl-TiO₂/mp-TiO₂, bl-TiO₂/mp-TiO₂/ZQDs and bl-TiO₂/mp-TiO₂/TQDs substrates, respectively. We extracted the statistical distribution diagrams of perovskite grain size by analyzing the top-view SEM images using the software named nano measurer. From the inset of the SEM images, the grain size is in Gaussian distribution, the average size is 254nm, 420nm and 430nm for perovskite grown on the bl-TiO₂/mp-TiO₂, bl-TiO₂/mp-TiO₂/ZQDs and bl-TiO₂/mp-TiO₂/TQDs substrates, respectively. It shows that the perovskite grain size on the QDs modified substrates is obviously larger than that on the counterpart. The enlargement of perovskite grain sizes may be ascribed to the following reasons: First, heterogeneous nucleation is suppressed and less drag force is performed from the QDs modified substrates, yielding increased nucleus spacing and promoted grain boundary migration in grain growth.¹⁸ Second, the QDs with high surface-to-volume ratio increase the contact area of perovskite/ETL, which is favorable for the formation of a high-quality film.⁹ Third, QDs offer added nucleation sites for perovskite, thus larger grain size can be obtained.¹² Considering that the grain boundaries and the defect density of the perovskite film can be reduced due to the enlarged grain size, leading to decreased non-radiative recombination and increased charge transport,^{19,20,21} this strategy would be beneficial for achieving high performance optoelectronic devices.

The XRD patterns of perovskite films on different mesoscopic layers are depicted in Figure 5. The stronger peaks of perovskite films coated on the QDs modified mp-TiO₂ layers indicate higher crystallinity, in line with the results taken from the SEM images above. Therefore, enhanced performances are expected for these QDs modified PSCs.

Then the subsequent HTM and Au electrode were spin coated and thermally evaporated on the perovskite layers, respectively, to form the complete PSC devices.

The device with bare mp-TiO₂ was marked as PT; the devices with ZQDs and TQDs modified mp-TiO₂ were marked as PZT and PTT, respectively. Cross-sectional SEM images show in Figure 4d, e, f indicate that the thickness of MAPbI₃ over ETLs is not changed significantly through QDs-treatment.

Figure 6. Statistical parameters of V_{oc} (a), J_{sc} (b), FF (c), and PCE (d) of PSCs based on ETL added with different amounts of ZQDs or TQDs. Each box summarizes the parameter distribution of 12 devices, in which the small square symbol (□) represents the mean and the line represents the median.

Figure 6 shows the statistical datas of PZT and PTT PSCs modified with different contents (0, 0.5, 1, 2, 4, 8 mg/ml) of ZQDs or TQDs. Here the PSCs with 0 mg/ml QDs are actually PT PSCs. Unexpectedly, as the concentration of QDs increases, the photovoltaic parameters of PZT and PTT PSCs appear different tendencies. Both circuit voltage (V_{oc}) and short circuit current (J_{sc}) of PTT decreased as the TQDs increased, which led to a linear reduction of PCE from 14.17% to 11.47% (1mg/ml), finally down to 6% (8 mg/ml). However, for the PZT PSCs, the V_{oc} slightly increased as ZQDs was loaded and remained stable. The average J_{sc} first increased from 20.59 mA cm⁻² to 22.71

mA cm^{-2} after loading 1mg/ml ZQDs, and then decreased. With the optimized loading amount of ZQDs, the average PCE of PSCs was enhanced from 14.17% to 16.96%.

Figure 7. (a) Typical J–V curves of champion PSCs via forward or reverse bias scanning; (b) the relation of output current density at maximum power point with time and (c) IPCE and integrated current data of corresponding devices; (d) The highest PCE for the devices based on PZT, PT and PTT structure when the mesoporous TiO_2 layer was operated at different spinning speed. All the measurements were performed using unsealed devices exposure to air with a relative humidity of $\approx 50\%$ – 65% .

Table 1. Summary of the photovoltaic performance parameters derived from the J-V curves presented in Figure 7a.

Sample	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF	PCE (%)
PZT (reverse)	1.02	22.79	0.74	17.20
PZT (forward)	1.01	22.69	0.66	15.13
PT (reverse)	1.00	20.77	0.70	14.54
PT (forward)	0.98	20.45	0.61	12.23

PTT (reverse)	0.97	18.69	0.65	11.78
PTT (forward)	0.93	18.43	0.50	8.57

Figure 7a shows the current density-voltage (J-V) curves of the champion PSCs. The photovoltaic parameters are recorded in Table 1. It shows that the champion PZT cell achieved a much higher PCE than that of the PTT cell and reference PT cell. Moreover, the PZT cells showed a smaller J-V hysteresis, which may resulted from the improved electron injection/transport to balance the hole flux at the anode.²² Figure 7b represented the steady current density at maximum power point as a function of time. The current density increased rapidly and then stabilized at 20.26, 19.13 and 16.66 mA cm⁻² for PZT, PT and PTT cells, respectively. Incident photon-to-current conversion efficiency (IPCE) results in Figure 7c showed that the PZT cell exhibited higher light response capacity over the entire wavelength range compared to the PT and PTT cells, which corresponded to the accelerated electron extract. Meanwhile, the integrated current density of the PZT, PT and PTT device was 21.6, 19.82 and 18.05 mA cm⁻² respectively, which was consistent with the J_{SC} extracted from their J-V curves. Moreover, the effect of mp-TiO₂ layer's thickness on the device efficiency was investigated. The thickness of mp-TiO₂ layers was controlled by changing the spin-coating speed from 2500 to 5000 rpm while keeping otherwise identical conditions. We found that the optimal spin-coating speed was 3000 rpm and the highest PCE values of the devices followed the sequence as PCE (PTT) < PCE (PT) < PCE (PZT) as before (Figure 7d).

Seen from Table 1, the value of V_{oc} was slightly changed, the change of PCE was mainly caused by J_{sc}. As a preliminary, we carried out the optical absorption studies. For PSCs, the strong capacity of light absorption plays an important role in high device performance. Seen from the results in Figure 8, the MAPbI₃ films exhibited a wide light absorbance range from the UV region to 800 nm. The MAPbI₃ film grown on the ZQDs modified mp-TiO₂ film (black curve) showed a considerable enhancement in UV-visible absorbance than the reference one (red curve), while the TQDs modified film (blue curve) showed a weakened light absorption.

Figure 8. UV/vis absorbance spectra of PZT, PT and PTT film.

Light absorption is strongly affected by the crystallinity, loading amount and surface coverage. The loading amount is decided by the thickness of capping layer and the infiltration of MAPbI₃ perovskite in mp-TiO₂ layer, which is determined by the morphology of the mesoporous layer.^{23,24} Though both top and cross-sectional SEM images of PZT and PTT showed that the crystallinity and thickness of capping layer of perovskite looked the same, the infiltration content was still unclear. Thus, a deep insight into the surface appearance of the pores before and after modification was performed subsequently. We checked the atomic force microscopy (AFM) micrographs of the bare mp-TiO₂ (a), ZQDs modified (b) and TQDs modified ones (c) as presented in Figure 9. It was observed that the mesoscopic TiO₂ particles were approximately spherical shape, randomly arranged and accompanied by the formation of a lot of large void spaces; the ZQDs (small bright spots) were extensively distributed on the surface of the mesoporous layer, resulting in less and smaller pores. However, the TQDs gathered at the surface of mp-TiO₂ particles and thus blocked most of the pores, mainly ascribed to the identical component between TQDs and the mp-TiO₂.

Figure 9. Top-view AFM images of (a) the pristine TiO₂, (b) the ZQDs modified TiO₂ and (c) the TQDs modified TiO₂ film; (d) N₂ adsorption-desorption isotherms and (e) BET surface area plot of the three kinds of mp-TiO₂. The AFM image sizes are all 1 × 1 μm.

The enhanced light absorption can help to explain the higher photocurrent and higher light harvesting efficiency in J-V curves above.²⁵ As no visible morphological difference was found between ZQDs-treatment and TQDs-treatment in the SEM top and cross-sectional images, the decreased light absorption for PTT film in Figure 8 (blue curve) may be ascribed to the reduced perovskite amount within the mesoporous layer caused by the blockage of pores.

Therefore, BET measurement was performed to investigate the pore volume and the specific surface area of the three samples. Figure 9d, e shows the N₂ adsorption-desorption isotherms and the corresponding BET surface area plots of mp TiO₂, ZQDs-mp TiO₂ and TQDs-mp TiO₂. The type IV (Brunauer -Deming Deming-Teller (BDDT) classification) isotherms for the above three samples indicated that mesopores were present. The type H3 hysteresis loops demonstrated the formation of slit-like pores, which were formed from the aggregation of the nanoparticles.²⁶ As the

pore volume directly determines the amount of MAPbI₃ within the mesoporous layer, the sharply decreased pore volume for the TQDs treated film will consequentially lead to the decreased fillers. Furthermore, the increased specific surface area of the oxides modified with ZQDs contributed to effective contact between MAPbI₃ and ETL, which is a significant player in the improved photovoltaic performance (Table 2).

Table 2. Summary of pore volume and BET surface area of mp TiO₂, ZQDs-mp TiO₂ and TQDs-mp TiO₂.

Sample	Pore volume (cm ³ /g)	BET surface area (m ² /g)
mp TiO ₂	0.475	55.962
ZQDs-mp TiO ₂	0.422	76.159
TQDs-mp TiO ₂	0.393	49.372

Figure 10. (a) PL spectra and (b) TRPL decay curves of the PT, PZT and PTT films; (c) the test Nyquist plots and the fitting curves of devices measured under ambient conditions in dark with a bias of 700 mV. The fitting curve is obtained according to the equivalent circuit in the inset.

In addition to the enhanced light absorption, we suspected that the ZQDs-treated mp-TiO₂ could improve the charge separation and extraction due to the increased contact interfaces. So, we conducted the steady-state photoluminescence (PL) and time-resolved PL (TRPL) measurements on the MAPbI₃ films with different mesoporous layer, as shown in Figure 10. All samples exhibited a PL peak at 770 nm (excitation wavelength 532 nm) derived from the perovskite, which was in agreement with the band edge emission from MAPbI₃ reported before.²⁷ Nevertheless, there existed great difference for the perovskite PL intensity among them. The PZT film exhibited a much

lower PL intensity than PT film, suggesting a less radiative recombination which may resulted from the increased electron extraction from MAPbI₃ to the electrode. Instead, the PTT film showed a much stronger PL intensity. To further study the difference of the behavior of excited electrons in the perovskite layer, TRPL measurements were performed. As displayed in Figure 10b, the average lifetimes of PT, PZT and PTT film were 21 ns, 14 ns and 28 ns, respectively, which were obtained by fitting the decay curves with a double-exponential function.²⁸ That is, the PZT sample exhibited the fastest PL quenching rate, which meant faster charge-carrier extraction across interface.^{29, 30} These results confirmed that the electron extraction was significantly speeded up by introducing ZQDs and the result was exactly opposite after replacing them with TQDs.

To further confirm the charge transfer at the perovskite / ETL interface, Nyquist plots in Figure 10c were recorded in dark over a frequency of 100 mHz to 1 MHz under an applied bias of 0.7 V. Seen from the Nyquist plots, a semicircle and an incomplete semicircle could be distinguished, which were corresponding to the charge transfer resistance (R_{tr}) and the recombination resistance (R_{rec}), respectively.³¹ Here we mainly focus on the R_{tr} by fitting the first semicircle at high frequency region using the equivalent circuit model (inset). The obviously different fitted R_{tr} values of PZT, PT and PTT were 14.4 k Ω , 19.9 k Ω and 29.9 k Ω , respectively. The smallest R_{tr} value of PZT indicated the most efficient charge transfer at the interface of ZQDs treated mp-TiO₂ and MAPbI₃, resulting in the highest J_{sc} of PSCs, in accordance with the results of PL experiments discussed above. Besides, the series resistances (R_s) of devices, originated from the external contacts, were 23.4 Ω , 30.3 Ω and 69.6 Ω for PZT, PT and PTT, respectively. The decrease of R_s also has a positive effect on FF,³² leading to a corresponding increase of PCE for PZT PSCs.

3. Conclusions

In short, we designed an improved mesoscopic PSC by inserting ZQDs, treated by a simple solution method, between perovskite and the mp-TiO₂ layer. With optimized

ZQDs modification contents, the PSC could achieve a greatly improvement in PCE, from 14.54% to 17.20%, due to the remarkable increase in J_{sc} . This result should be attributed to the enhanced light absorption of perovskite film, improved electron extraction capability and well-matched energy levels. After replacing ZQDs with TQDs who have similar size with ZQDs and the same component with mp-TiO₂, the device performance was deteriorated owing to the sharply decreased specific surface area because of the aggregation of TQDs. The results provide us an efficient and facile way to speed up the electron transport from the perovskite absorber to the current collector and to improve the photovoltaic performance of mesoscopic PSCs.

Conflicts of interest

There is no conflict to declare.

Acknowledgements

This work is financially supported by the Talent Fund of Hubei University of Technology (Grant No. BSQD2020107), National Key R&D Program of China (Grant No. 2017YFB0406405), Science and Technology Research Project of Education Department of Hubei Province (Q20201402), they are greatly acknowledged. We also acknowledge the assistance from the Analytical and Testing Center of HUST.

Appendix A. Supplementary data

Supplementary data to this article is available.

References

- [1] Kojima A, Teshima K, Shirai Y, et al. O-rganometal halide perovskites as visible-light sensitizers for photovoltaic cells. *J Am Chem Soc* 2009, **131**:6050-6051.
- [2] Zhang T, Wu J, Zhang P, et al. High Speed and stable solution-processed triple cation perovskite photodetectors. *Adv Opt Mater* 2018, **6**:1701341.
- [3] NREL, <https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies>.

20200925. pdf (accessed: September 2020).

- [4] Gratzel M. The light and shade of perovskite solar cells. *Nat Mater* 2014, **13**:838-842.
- [5] Guillén E, Ramos FJ, Anta JA, et al. Elucidating Transport-Recombination Mechanisms in Perovskite Solar Cells by Small-Perturbation Techniques. *J Phy Chem C* 2014,**118**:22913-22922.
- [6] Heo JH, You MS, Chang MH, et al. Hysteresis-less mesoscopic $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite hybrid solar cells by introduction of Li-treated TiO_2 electrode. *Nano Energy* 2015,**15**:530-539.
- [7] Kim HS, Lee JW, Yantara N, et al. High efficiency solid-state sensitized solar cell-based on submicrometer rutile TiO_2 nanorod and $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite sensitizer. *Nano Lett* 2013, **13**:2412-2417.
- [8] Son D-Y, Im J-H, Kim H-S, et al. 11% Efficient Perovskite Solar Cell Based on ZnO Nanorods: An Effective Charge Collection System. *J Phy Chem C* 2014, **118**:16567-16573.
- [9] Xiong Y, Liu Y, Lan K, et al. Fully printable hole-conductor-free mesoscopic perovskite solar cells based on mesoporous anatase single crystals. *New J Chem* 2018, **42**:2669-2674.
- [10] Garcia VJ, Pelicano CM, Yanagi H. Low temperature-processed ZnO nanorods- TiO_2 nanoparticles composite as electron transporting layer for perovskite solar cells. *Thin Solid Films* 2018, **662**:70-75.
- [11] Seo JY, Uchida R, Kim HS, et al. Boosting the efficiency of perovskite solar cells with CsBr-modified mesoporous TiO_2 beads as electron-selective contact. *Adv Funct Mater* 2018, **28**:1705763.
- [12] Chen W, Li K, Wang Y, et al. Black Phosphorus Quantum Dots for Hole Extraction of Typical Planar Hybrid Perovskite Solar Cells. *J Phys Chem Lett* 2017, **8**:591-598.
- [13] Zeng X, Zhou T, Leng C, et al. Performance improvement of perovskite solar cells by employing a CdSe quantum dot/PCBM composite as an electron transport layer.

- J Mater Chem A* 2017, **5**:17499-17505.
- [14] Ryu J, Lee JW, Yu H, et al. Size effects of a graphene quantum dot modified-blocking TiO₂ layer for efficient planar perovskite solar cells. *J Mater Chem A* 2017, **5**:16834-16842.
- [15] Li H, Shi W, Huang W, et al. Carbon Quantum Dots/TiO₂ Electron Transport Layer Boosts Efficiency of Planar Heterojunction Perovskite Solar Cells to 19%. *Nano Lett* 2017, **17**:2328-2335.
- [16] Zhang Q, Dandeneau CS, Zhou X, et al. ZnO Nanostructures for Dye-Sensitized Solar Cells. *Adv Mater* 2009, **21**:4087-4108.
- [17] Park K, Zhang Q, Garcia BB, et al. Effect of an Ultrathin TiO₂ Layer Coated on Submicrometer-Sized ZnO Nanocrystallite Aggregates by Atomic Layer Deposition on the Performance of Dye-Sensitized Solar Cells. *Adv Mater* 2010, **22**:2329-2332.
- [18] Bi C, Wang Q, Shao Y, et al. Non-wetting surface-driven high-aspect-ratio crystalline grain growth for efficient hybrid perovskite solar cells. *Nat Commun* 2015, **6**:7747.
- [19] Liu D, Wu L, Li C, et al. Controlling CH₃NH₃PbI_{3-x}Cl_x Film Morphology with Two-Step Annealing Method for Efficient Hybrid Perovskite Solar Cells. *ACS Appl Mater Inter* 2015, **7**:16330-16337.
- [20] Zhou H, Chen Q, Li G, et al. Interface engineering of highly efficient perovskite solar cells. *Science* 2014, **345**:542-546.
- [21] Wang Y, Wu J, Zhang P, et al. Stitching triple cation perovskite by a mixed anti-solvent process for high performance perovskite solar cells. *Nano Energy* 2017, **39**:616-625.
- [22] Yang D, Zhou X, Yang R, et al. Surface optimization to eliminate hysteresis for record efficiency planar perovskite solar cells. *Energy Environ Sci* 2016, **9**:3071-3078.
- [23] Leijtens T, Lauber B, Eperon GE, et al. The importance of perovskite pore filling in organometal mixed halide sensitized TiO₂-based solar cells. *J Phy Chem Lett*

- 2014, **5**:1096-1102.
- [24] Yin J, Cao J, He X, et al. Improved stability of perovskite solar cells in ambient air by controlling the mesoporous layer. *J Mater Chem A* 2015, **3**:16860-16866.
- [25] Chen Y, Chen T, Dai L. Layer-by-Layer Growth of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ for Highly Efficient Planar Heterojunction Perovskite Solar Cells. *Adv Mater* 2015, **27**:1053-1059.
- [26] Wang G, Zhu X, Yu J. Bilayer hollow/spindle-like anatase TiO_2 photoanode for high efficiency dye-sensitized solar cells. *J Power Sources* 2015, **278**:344-351.
- [27] Xie Y, Shao F, Wang Y, et al. Enhanced performance of perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cell by using $\text{CH}_3\text{NH}_3\text{I}$ as additive in sequential deposition. *ACS Appl Mater Inter* 2015, **7**:12937-12942.
- [28] Wang J, Cao R, Da P, et al. Purcell effect in an organic-inorganic halide perovskite semiconductor microcavity system. *Appl Phy Lett* 2016, **108**:022103.
- [29] Zheng X, Wei Z, Chen H, et al. Designing nanobowl arrays of mesoporous TiO_2 as an alternative electron transporting layer for carbon cathode-based perovskite solar cells. *Nanoscale* 2016, **8**:6393-6402.
- [30] Li S, Zhang P, Wang Y, et al. Interface engineering of high efficiency perovskite solar cells based on ZnO nanorods using atomic layer deposition. *Nano Res* 2017, **10**:1092-1103.
- [31] Christians JA, Fung RC, Kamat PV. An inorganic hole conductor for organo-lead halide perovskite solar cells. Improved hole conductivity with copper iodide. *J Am Chem Soc* 2013, **136**:758-764.
- [32] Juarez-Perez EJ, Wußler M, Fabregat-Santiago F, et al. Role of the selective contacts in the performance of lead halide perovskite solar cells. *J Phy Chem Lett* 2014, **5**:680-685.

Figures

Figure 1

Fabrication process of QDs modified PSCs.

Figure 2

XRD testing results of (a) ZQDs and (b) TQDs; TEM and HRTEM (inset) image of (c) ZQDs and (d) TQDs; (e) distribution of Zn in ZQDs/mp-TiO₂ sample obtained from the cross section-scan analysis of EDS mapping images and the corresponding cross section SEM image.

Figure 3

Diagram of energy levels in the ZQDs or TQDs modified device.

Figure 4

Top-view FESEM images of perovskite crystals grown on (a) the pristine mp-TiO₂, (b) the ZQDs modified mp-TiO₂ and (c) the TQDs modified mp-TiO₂ film; Cross-sectional SEM images of a complete device based on the (d) PT, (e) PZT and (f) PTT structure. Insets are the grain size distributions of perovskite. The scale bars for all SEM images are 200 nm.

Figure 5

XRD testing results of perovskite films on original TiO₂, the ZQDs treated TiO₂ and the TQDs treated TiO₂ layer.

Figure 6

Statistical parameters of Voc (a), Jsc (b), FF (c), and PCE (d) of PSCs based on ETL added with different amounts of ZQDs or TQDs. Each box summarizes the parameter distribution of 12 devices, in which the small square symbol (⊠) represents the mean and the line represents the median.

Figure 7

(a) Typical J–V curves of champion PSCs via forward or reverse bias scanning; (b) the relation of output current density at maximum power point with time and (c) IPCE and integrated current data of corresponding devices; (d) The highest PCE for the devices based on PZT, PT and PTT structure when the mesoporous TiO_2 layer was operated at different spinning speed. All the measurements were performed using unsealed devices exposure to air with a relative humidity of $\approx 50\%$ – 65% .

Figure 8

UV/vis absorbance spectra of PZT, PT and PTT film.

Figure 9

Top-view AFM images of (a) the pristine TiO_2 , (b) the ZQDs modified TiO_2 and (c) the TQDs modified TiO_2 film; (d) N_2 adsorption-desorption isotherms and (e) BET surface area plot of the three kinds of mp- TiO_2 . The AFM image sizes are all $1 \times 1 \mu\text{m}$.

Figure 10

(a) PL spectra and (b) TRPL decay curves of the PT, PZT and PTT films; (c) the test Nyquist plots and the fitting curves of devices measured under ambient conditions in dark with a bias of 700 mV. The fitting curve is obtained according to the equivalent circuit in the inset.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [GraphicalAbstract.tif](#)
- [SupportingInformationforPublication.pdf](#)